On the Enantiomorphism of Organic Peroxy Compounds in the Crystalline State

Sir:

Because of the dihedral angle of the peroxy group, a molecule of an organic peroxy compound is not identical with its mirror image. In solution, the low barrier[1] to rotation about the peroxy link results in frequent interconversion between the mirror-related configurations, so that although nonzero dipole moments have been reported,[2] D,L isomerism has not. In the crystalline solid, this is not so, and we have found by X-ray structure analysis both enantiomorphic and racemate crystal structures.

In the crystal structure of dibenzoyl peroxide we find a peroxy dihedral angle of 93°. The crystals have the space group $P2_12_12_1$ and the molecules in any one crystal are all of the same sense. The same is probably true for the crystals of *p*-nitroperoxybenzoic acid, which also have the symmetry $P2_12_12_1$.

In the crystal structures of peroxypelargonic acid and *o*-nitroperoxybenzoic acid,[3] on the other hand, there are equal numbers of left and right handed molecules. In the fatty peroxy acid crystals, the molecules of the same sense are hydrogen bonded in spirals and there are an equal number of left and right handed spirals. In the *o*-nitroperoxybenzoic acid alternate left and right handed molecules form a hydrogen-bonded chain. In the latter structure all the hydrogen atoms were directly located and the dihedral angle was found to be 146°.

Thus we have observed two examples of each of the enantiomorphic and racemate type of crystal structures in the four compounds we have studied. Which crystal forms, for any particular compound, will depend on whether the assemblage of like or of unlike molecules has the greater lattice energy at the temperature of the crystallization. No other crystal structure analyses of organic peroxides have been reported. It is interesting to note, however, that hydrogen peroxide itself has an enantiomorphic crystal structure in space group $P4_12_12$,[4] while the hydrogen peroxide dihydrate structure is centrosymmetrical.[5]

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